ORGANOSILICON COMPOUNDS

XXXVI[*]. THE PREPARATION OF SOME PHOSPHORUS-SUBSTITUTED PHENYLTRIMETHYLSILANES

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We describe below the preparation of some new substituted phenyltrimethylsilanes, *m*- and *p*-$XC_6H_4SiMe_3$, required for kinetic studies, in which X = $P(O)Ph_2$, $P(O)Me_2$, $P(O)(OEt)_2$, $P(O)(OH)_2$, $P(O)Cl_2$, $OP(O)(OEt)_2$, $CH_2P(O)(OEt)_2$, $CH_2P(O)(OH)_2$, and $Me_3P^+I^-$.

EXPERIMENTAL

Diethyl m- and p-(trimethylsilyl)phenylphosphonate

The Grignard reagent prepared in tetrahydrofuran from (*p*-chlorophenyl)trimethylsilane (87 g, 0.50 mole) and magnesium (12.2 g, 0.50 g-atom) was added slowly to diethyl phosphorochloridate (77.4 g, 0.45 mole) in diethyl ether (150 ml). The mixture was refluxed for 1 h and allowed to cool, and was then treated with cold dilute sulphuric acid. Ether extraction was followed by washing (2 *N* NaOH, then water) and drying (Na_2SO_4) of the extract, removal of the solvent, and rapid distillation of the residual oil. Fractionation of the distillate gave diethyl *p*-(trimethylsilyl)phenylphosphonate (78 g, 60 %), b.p. 154–156°/2.5 mm, n_D^{25} 1.4933. (Found: C, 54.7; H, 8.2. $C_{13}H_{23}O_3PSi$ calcd.: C, 54.55; H, 8.05 %.)

The *meta*-isomer, b.p. 142–143°/2.2 mm, n_D^{25} 1.4915, was similarly prepared in 60 % yield. (Found: C, 54.1; H, 7.8 %.)

m- And p-(trimethylsilyl)phenylphosphonic dichloride

Diethyl *p*-(trimethylsilyl)phenylphosphonate (14.2 g, 0.050 mole) was refluxed with phosphorus pentachloride (20.8 g, 0.10 mole) for 2 h. Distillation gave phosphoryl chloride followed by *p*-(trimethylsilyl)phenylphosphonic dichloride (9.5 g, 70 %), b.p. 124–128°/1.12 mm, which solidified to give crystals of m.p. 44–45°. (Found: C, 38.8; H, 4.7; Cl, 26.7. $C_9H_{13}Cl_2OPSi$ calcd.: C, 40.4; H, 4.8; Cl, 27.1 %.)

Similarly prepared in 66 % yield was the *meta*-isomer, b.p. 131–132°/2.5 mm, n_D^{25} 1.5352. (Found: Cl, 26.5 %.)

m- And p-(trimethylsilyl)phenylphosphonic acid

To a solution of *p*-(trimethylsilyl)phenylphosphonic dichloride (4 g) in acetone

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(10 ml) was added sufficient 2 *N* aqueous sodium hydroxide to give a clear solution. The mixture was acidified, and the precipitate was taken up in ether and recovered by evaporation of the ether. Three recrystallizations from light petroleum (b.p. 60–80°) gave *p*-(trimethylsilyl)phenylphosphonic acid, m.p. 174–175°. (Found: C, 46.5; H, 6.3. $C_8H_{13}O_3PSi$ calcd.: C, 46.95; H, 6.5 %.)

The *meta*-isomer, m.p. 96–98°, was prepared similarly. (Found: C, 46.7; H, 6.4 %.)

Diphenyl[p- and m-(trimethylsilyl)phenyl]phosphine oxide

p-(Trimethylsilyl)phenylphosphonic dichloride (5.5 g, 0.022 mole) in ether (20 ml) was added to the Grignard reagent from bromobenzene (9.4 g, 0.060 mole) and magnesium (1.44 g, 0.060 g-atom) in ether, and the mixture was refluxed for 2 h. The usual working-up gave an oil which crystallized slowly. Recrystallization from light petroleum (b.p. 60–80°) gave impure material of m.p. 75–80°, and so the solution in light petroleum was chromatographed on alumina with benzene and 6:1 benzene/methanol as eluants. Recrystallization from light petroleum then gave diphenyl[*p*-(trimethylsilyl)phenyl]phosphine oxide (5 g), m.p. 93°. (Found: C, 72.0; H, 6.7. $C_{21}H_{23}OPSi$ calcd.: C, 72.0; H, 6.6 %.)

A similar procedure gave the *meta*-isomer, b.p. 212–215°/0.1 mm, as a glass, which crystallized after several months. (Found: C, 72.0; H, 6.5 %.)

Dimethyl[p-(trimethylsilyl)phenyl]phosphine oxide

p-(Trimethylsilyl)phenylphosphonic dichloride (34 g, 0.125 mole) in a little ether was added to the Grignard reagent made from methyl iodide (42.6 g, 0.30 mole) and magnesium (7.5 g, 0.31 g-atom) in ether, and the mixture was refluxed for 2 h. Addition of dilute sulphuric acid gave two organic layers, and the lower of these was separated and dissolved in chloroform. The chloroform solution was washed, dried (Na_2SO_4), and evaporated to leave a yellow oil which slowly solidified. Recrystallization from light petroleum gave dimethyl[*p*-(trimethylsilyl)phenyl]phosphine oxide (12 g, 43 %), m.p. 114°. (Found: C, 58.1; H, 8.3. $C_{11}H_{19}OPSi$ calcd.: C, 58.35; H, 8.4 %.)

Trimethyl[m- and p-(trimethylsilyl)phenyl]phosphonium iodide and hydroxide

A solution of dimethyl[*p*-(trimethylsilyl)phenyl]phosphine oxide (5.8 g, 0.025 mole) in benzene (40 ml) was added to lithium aluminium hydride (1.9 g, 0.05 mole) in di-*n*-butyl ether (40 ml). The mixture was stirred and refluxed under nitrogen for 3 h, then cooled and treated carefully with cold dilute aqueous sodium hydroxide. The organic layer was separated and filtered under nitrogen, and the solvent was removed to leave an oil. This was dissolved in benzene, and methyl iodide was added. The solid which formed was recrystallized from chloroform/light petroleum (b.p. 60–80°) to give trimethyl[*p*-(trimethylsilyl)phenyl]phosphonium iodide (55 %), m.p. 183–184°. (Found: C, 40.7; H, 6.25. $C_{12}H_{22}IPSi$ calcd.: C, 40.9; H, 6.25 %.)

[The iodide was converted into the hydroxide by boiling with an aqueous suspension of silver oxide. The solution was filtered, and the filtrate was concentrated on a rotary evaporator to leave an oil which was crystallized by concentration of its solution in ethanol. Several repetitions of the crystallization left a white crystalline hygroscopic material which was used without further purification.]

The *meta*-isomer of the iodide, m.p. 173° from the impure phosphine oxide, was prepared analogously, but with recrystallization from ethyl acetate, in 40 % yield. (Found: C, 40.8; H, 6.4 %.)

Diethyl m- and p-(trimethylsilyl)phenyl phosphate

Sodium (4.14 g, 0.18 g-atom) was dissolved in ethanol (60 ml) and *p*-(trimethylsilyl)phenol (30 g, 0.18 mole) in ethanol (60 ml) was added, followed by diethyl phosphorochloridate (30.0 g, 0.18 mole) in benzene (60 ml). The mixture was refluxed for 3 h then added to water. Ether extraction followed by washing and drying (Na_2SO_4) of the extract, and removal of the ether left a liquid which was fractionated to give diethyl *p*-(trimethylsilyl)phenyl phosphate (20 g, 45 %), b.p. 145–150°/2–2.5 mm, n_D^{25} 1.4840. (Found: C, 52.4; H, 7.7. $C_{13}H_{23}O_4PSi$ calcd.: C, 51.8; H, 7.6 %.)

The *meta*-isomer, b.p. 148–150°/1.0 mm, n_D^{25} 1.4900, was prepared analogously in 50 % yield. (Found: C, 51.3; H, 7.4 %.)

Diethyl m- and p-(trimethylsilyl)benzylphosphonate

Sodium (4.6 g, 0.20 g-atom) was dissolved in a mixture of diethyl phosphonate (28 g, 0.21 mole) and light petroleum (b.p. 60–80°) (50 ml). *p*-(Trimethylsilyl)benzyl bromide (37.0 g, 0.18 mole) was added, and the mixture was refluxed for 6 h. Removal of the precipitated sodium bromide, followed by fractionation, gave diethyl *p*-(trimethylsilyl)benzylphosphonate (30 g, 55 mole), b.p. 151–153°/1.0 mm, n_D^{25} 1.4897. (Found: C, 55.9; H, 8.6. $C_{14}H_{25}O_3PSi$ calcd.: C, 55.9; H, 8.3 %.)

The *meta*-isomer, b.p. 149–151°/2.3 mm, n_D^{25} 1.4885, was prepared analogously in 60 % yield. (Found: C, 55.3; H, 8.1 %.)

m- And p-(trimethylsilyl)benzylphosphonic acid

Diethyl *p*-(trimethylsilyl)benzylphosphonate (10.0 g, 0.033 mole) was refluxed for 4 h with phosphorus pentachloride (13.5 g, 0.066 mole). After removal of phosphoryl chloride, the residue was fractionated to give a liquid (*ca.* 4 g) of b.p. 150°/2 mm, which was assumed to be the acid chloride. This was dissolved in acetone and treated with sufficient 2 *N* aqueous sodium hydroxide to give a clear solution, which was then acidified. Ether extraction followed by removal of the ether left a solid which was recrystallized to give *p*-(trimethylsilyl)benzylphosphonic acid (25 %), m.p. 167–168°. (Found: C, 48.9; H, 7.0. $C_{10}H_{17}O_3PSi$ calcd.: C, 49.15; H, 7.0 %.)

The *meta*-isomer, m.p. 144°, was prepared analogously in similar yield. (Found: C, 49.0; H, 6.9 %.)

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SUMMARY

We have prepared some substituted phenyltrimethylsilanes, *m*- and *p*-$XC_6H_4SiMe_3$, in which X = P(O)Ph_2, P(O)Me_2, P(O)$(OEt)_2$, P(O)$(OH)_2$, P(O)Cl_2, OP(O)$(OEt)_2$, $CH_2P(O)(OEt)_2$, $CH_2P(O)(OH)_2$ and $Me_3P^+I^-$.